STUDIES ON THE HEAVY METALS INTERACTIONS WITH SOILS AND CROPS

DISSERTATION SUBMITTED FOR THE DEGREE OF

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IN

CHEMISTRY

BY

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This is to certify that the dissertation entitled, 'Studies on the heavy metals interactions with soils and crops' is an original work of Mr. Mohd. Aslam Qureshi and is suitable for submission for the degree of Master of Philosophy in Chemistry.

(SAMIULLAH KHAN)
Supervisor

A C K N O W L E D G E M E N T

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MOHD. ASLAM QURESHI

C O N T E N T S

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C H A P T E R - I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

DEFINITION

Soil may be defind as occupying the outermost part of the earth's crust and possessing distinct morphological, mineralogical, chemical and physical properties resulting from certain inheritant factors, from its unique position on the surface of crust and from the environmental factors existing at that position.

Soils are formed by the natural process of disintegration of rocks and organic matter under various climatic conditions. Soils are consists of five main components, namely clay minerals, organic matter, soil water, soil air and living organisms.

CLAY MINERALS

The mineral matter, a product of physical and chemical weathering of rocks consists of particles of varying sizes, those in the finer state of subdivision (< 0.002 mm) form the clay fractions of the soil. The properties of soils are determined more by the type of the clay mineral fraction present than any other constituent of soil material. The crystal structure of clay minerals have been discussed in considerable detail by Marshall (1935) Hendricks (1942), Marshall (1964) etc.

X.ray and other studies have revealed that clays are crystalline in nature and composed of few simple building units (Hidding, 1923). The clays are composed of alternately parallel two dimensional layers of silica tetrahedron and alumina octahedron sheets (Hidding, 1923). The important clay minerals which are commonly distributed in soils are as follows :

a) KAOLINITE

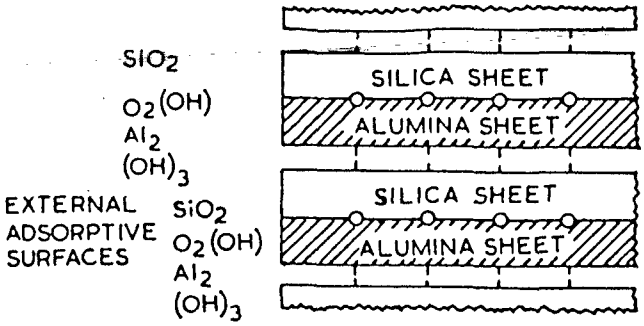
Kaolinites are hydrous aluminium silicates and composed of an alternate combination of a single tetrahedral sheet of silica and a single octahedral sheet of alumina in such a way that the tips of silica tetrahedral and a layer of octahedral sheet form a common layer. Thus it has a 1:1 non-expanding lattice where two adjacent sheets are held up together by hydrogen bonding. The have such a strong hydrogen bonding that they do not allow water to penetrate between the layers. Thus, these clays have little swelling, plasticity, cohesion and shrinkage properties. The structural formula of kaolinite is $(OH)_8Si\ Al_4O_{10}$. The size of the unit cell is $7.2A^{o}$. Vide Fig. 1(a) and 2(a).

b) MONTMORILLONITE

Montmorillonites are swelling and sticky clays. They have 2:1 arrangement in which a single tetrahedral layer

SILICA SHEET

ALUMINA SHEET



CRYSTAL UNIT
7.1

DISTANCE FIXED
LITTLE OR NO ADSORPTION

CRYSTAL UNIT

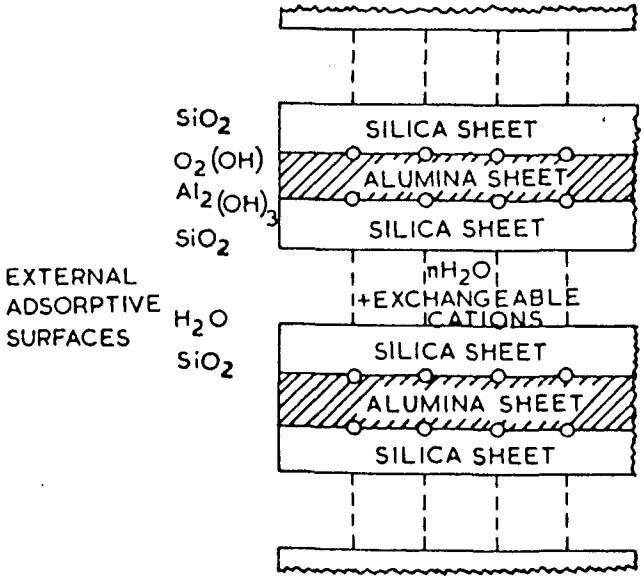
I(a) DIAGRAMMATIC EDGE VIEW OF KAOLINITE SHOWING TWO COMPLETE LAYERS. THE RESPECTIVE CRYSTAL UNITS ARE BOUND TO EACH OTHER TIGHTLY BY AN OXYGEN-HYDROXYL LINKAGE, THEREBY GIVING A RESTRICTED AND NON-EXPENDING LATTICE. THE ADSORPTIVE CAPACITY IS LIMITED.

I(c) ILLITE HAS THE SAME GENERAL STRUCTURAL ORGANIZATION AS MONTMORILLONITE EXCEPT IN RESPECT TO THE LINKAGES BETWEEN THE CRYSTAL UNITS. HERE K ATOMS SUPPLY ADDITIONAL CONNECTING LINKAGES BETWEEN THE CRYSTAL UNITS, THUS SUPPLEMENTING THE OXYGEN BONDING. THE EXPANSION IS SHARPLY LASSENED BY K LINKAGES AND ADSORPTIVE CAPACITY OF THE CLAY LOWERED.

CRYSTAL UNIT
9.3 A

DISTANCE VARIABLE
INTERNAL ADSORPTIVE SURFACES

CRYSTAL UNIT



I(b) DIAGRAMMATIC EDGE VIEW OF MONTMORILLONITE SHOWING TWO COMPLETE LAYERS. THE RESPECTIVE CRYSTAL UNITS ARE LOOSELY BOUND TO ONE ANOTHER BY WEAK OXYGEN LINKAGES WHICH ALLOW WIDE EXPANSION OF THE LATTICE. THERE IS HIGH INTERNAL ADSORPTION OF WATER AND CATIONS.

FIG. 1

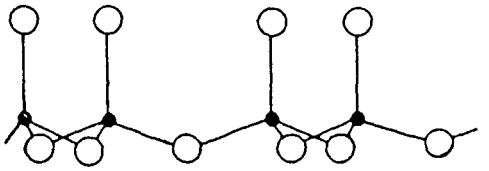
joined to each side of the octahedral layer in sandwitch fashion by sharing of oxygen atoms.

Marshall (1935) and Hendricks (1942) showed that montomorillonite always differs from its theoretical formula $(OH)_4\ Si_8Al_4O_{20}$, nH_2O because of substitution within the lattice of Al by Mg, Fe, Zn and Cr etc and Si by Al or P, giving a series of group minerals.

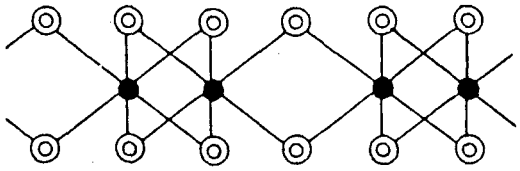
X.ray studies have shown the stacking of silica-alumina-silica in the C.direction, layers being continuous in a-, and b- direction with the result that these exert a weak bond and an excellent cleavage between them, Water and other polar molecules can easily penetrate between the unit layer causing the lattice to expand in the C-direction. The dimension of C-axis is, therefore, not fixed but varies from 9.6A^o to substantially complete separation of the individual layers in some cases vide figs I(b) 2(b). The cation exchange capacity of this mineral is high and varies from 80 to 120 meq. per 100 g clay.

c) ILLITE

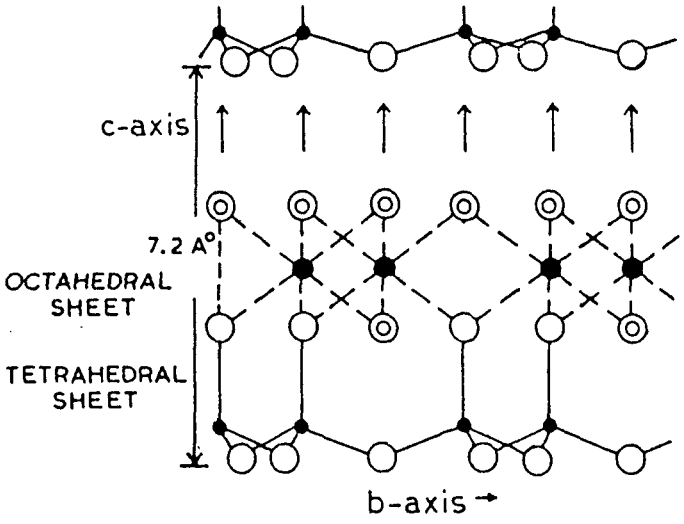
Illite has very similar structure to that of monto-morillonite having 2:1 type of basic unit structural arrange-ment (Grim et al. 1937). However, it has large number of potassium ions between the silica sheets of two successive units that act as a bridge in holding adjacent layers



TETRAHEDRAL SILICON SHEET



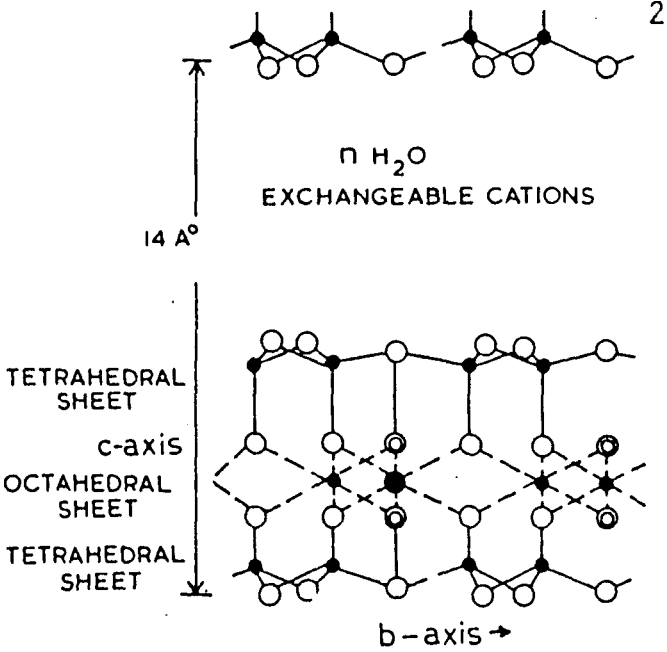
OCTAHEDRAL GIBBSITE SHEET



HYDROGEN BONDING	
6 (OH)	— 6
4 Al	+12
4 O+2 (OH)	—10
4 Si	+16
6 O	—12
NET CHARGE	0

2(a) KAOLINITE, A 1:1 LAYER SILICATE MINERAL

2(c) ILLITE STRUCTURE IS SIMILAR TO 2(b) EXCEPT THAT THE ELECTRICAL IMBALANCE IS SET RIGHT BY THE PRESENCE OF K IONS SITUATED BETWEEN ADJACENT LAYERS SO THAT THE NET CHARGE IS O.



6 O	−12
4 (Si, Al)	+16 or less
4 O+2 (OH)	−10
4 (Al, Fe, Mg)	+12 or less
4 O+2 (OH)	−10
4 Si	+16
6 O	−12
NET CHARGE	O or less e.g.-1

2(b) MONTMORILLONITE, A FREELY EXPANSIBLE 2:1 LAYER MINERAL. THE INTER-LAYER CATIONS ARE FREELY EXCHANGEABLE.

FIG. 2

together so tightly that water cannot penetrate between them. The formula proposed by Hendricks and Ross (1941) for illite $_{18}(OH)_4$ $(KCa\frac{1}{2}Na)_{1.68}$ $(Si_{7.30}Al_{0.70})$ $(Al_{0.94}$ $Fe^{3+}_{1.94}Fe^{2+}_{0.38}Mg^{2+}_{0.8})$ O_{20}. Amorphous substitution is possible within the lattice resulting in wide variation in their composition. Because of its close resemblance with mica, it is considered to be a member of mica group. The cation exchange capacity of illite varies from 20 to 40 meq. per 100 g clay.

d) VERMICULITE

The structure of vermiculite was first studied by Gruner (1934) and latter modified by Hendricks and Jofferson (1938). The structure is similar to illite but two layers held more weakly bound to gether by hydrated magnesium (6 water molecules in octahedral Co-ordination with Mg) rather than tightly bound K^+ ions as in illite. A general formula for natural vermiculite is $(OH)_4$ (Mg, Ca) $(Si_{8-X}Ax)$ $(Mg.Fe)_6O_{20}$. Y H_2O where X=1 to 1.4 and γ = about 8. It has more swelling property than illite but not as much as montmorillonite.

e) CHLORITE

The structure of chlorite is given by Donahue (1977). It is often called 2:2 type clay because it is similar to the unit lattice of vermiculite except that hydrated magnesium

in Vermiculite is a firmly bonded magnesium hydroxide octahedral sheet in chlorite. Chlorites do not swell when wetted with water and have low cation exchange capacity varying from 10 to 40 meq per 100 g clays.

f) AMORPHOUS CLAYS

Amorphous clays are the mixture of silica and alumina, containing weathered oxides of iron etc. that have not formed well oriented crystals. These are common in soils and exists in varying proportions. Their properties are usually uncommon such as positive charge or anion exchange property that depends upon the pH and the salt solution of the soil.

SOIL ORGANIC MATTER (SOM)

The soil organic matter (SOM) or humus, a component of the soil may be defind as the organic residue left behind after microbial decomposition of plant and animal remains, frequently dark coloured and possessing certain characteristics in its physical and chemical properties (Waksman, 1938). Its synthesis and degradation constitute a dynamic process and depends largely on soil environment. In general, humus may be divided into two main groups as follows :

a) HUMIC SUBSTANCES - Transformed products bearing little or no resemblance to the anatomical structures from which they are derived. The humic substances can further be subdivided into three main groups namely :

i) Humic acid - Soluble in alkali but Insoluble in acids.

ii) Fulvic acid - Soluble in both alkali and acids

iii) Humin - Insoluble in both alkali and acids.

During the last two decades, accumulation patterns of humic and fulvic acids has extensively been studied by various workers (Syers et al. 1970, Schnitzer and Khan, 1972, Ghosh and Schnitzer, 1980).

The chemistry of humic substances has been studied in recent years(Wilson and Goh, 1983, Wilson et. al. 1983, Newman and Tate, 1984) to characterize their composition and properties in soil.

Various degradative and nondegradative methods have been employed which reveal that the major functional groups in humic materials are those containing carboxyl, methoxy, amine ($-NH_2$), Secondary amino (-NH-) and ring nitrogen. The presence of large concentration of oxygen containing groups (-COOH, -OH and -C=O) in humic materials tends to

make them hydrophilic. While the presence of aromatic rings, and aliphatic carbons provide them a hydrophobic nature. Thus, the humic materials are considered to have a simultaneous hydrophilic as well as hydrophobic nature and hence capable of adsorption of hydrophobic and hydrophilic substances on its surfaces.

On the basis of numerous analysis made on humic and fulvic acids, the main differences between model HA and FA were reported (Schnitzer and Ghosh, 1979) as follows : Total acidity, alcoholic OH, and -COOH contents of the FA are appreciably higher than HA while the number of phenolic -OH, total -C=O and $-OCH_3$ groups are approximately same in both the substances.

The partial chemical structure of fulvic acid as proposed by Schnitzer and Ghosh (1979) shown in fig. 3.

It illustrates the importance of hydrogen bonding besides the Vander Wall's and $\pi-\pi$ bonding. It has also been reported by Zyrin, (1948) that a part of humic substance known as humin, consists of humic and fulvic acids. Besides, the humic and fulvic acid content, hymatomelanic acid is an additional constituent in humin fraction (Banerjee and Mukherjee, 1972).

Besides the humic substances, certain other organic compounds such as aliphatic and aromatic acids, amino acids,

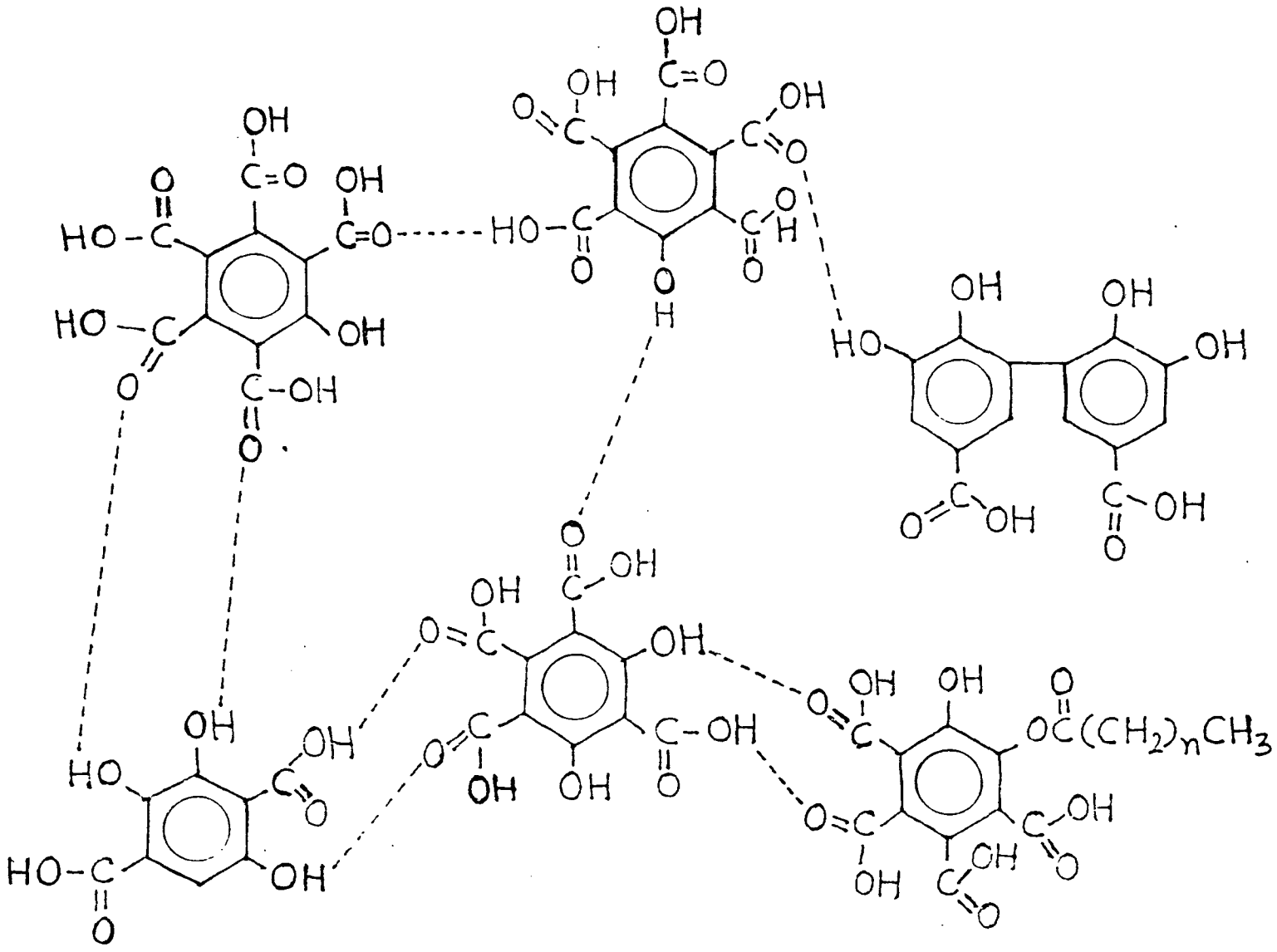


FIG. 3. PARTIAL CHEMICAL STRUCTURE OF FULVIC ACID.

polysacharides and some other substances have been reported to link with humic acid in soil. (Bondietti et. al. 1972, Kononova, 1972).

SOIL WATER

Soil water is an important constituent of soil which helps to control soil,air, soil temperature, evapotranspiration requirement and supply of nutrients to growing plants (Brady, 1974). The soil water content vary with the soil texture and vary from 5.1 to 11.9 percent (Donahue, 1977). The amount of available water in soil was found to be related with silt (Abral and Bhumbla, 1966) and Organic matter content (Ali, 1965). The movement of water in soil is influenced by the location, extent, and physical characteristics of the different horizons.

SOIL AIR

The soil air mainly consists of oxygen, carbondioxide, nitrogen and nitrous oxide etc. It has been observed that the composition of soil air varied with the climatic conditions (Russell and Apple yard, 1915) as well as with the nature of the soil (Jong 1981. Some of physiologically active gases like ethylene, methane, hydrogen sulphide have been reported to be formed in water logged soils by microorganisms (Smith, 1977).

LIVING ORGANISM IN SOIL

During the last four decades it has definitely established that the soil is characterized by a distinct microbiological population made up of specific groups. Small living things (microbials or microorganism) are biologically classified as plant (microflora), animal (microfauna) and are considered to be present in soil surfaces or in top few inches of the soil having their population in billions per gram of soil (Donahue, 1977).

i) BACTERIA

Bacteria are most abundently present in soils. These are unicellular organism and include spore forming and non-spore forming rods, cocci, vibrio and spirilla.

They vary considerably in shape, size, oxygen requirements (aerobic and anaerobic), energy utilization (autotrophic and heterotrophic) and relation to plants and animals (Saprophytic and parasitic).

ii) FUNGI

These include a large group of organisms known as phycomycetes, ascomycetes, hypomycetes and basidomycetes. Their classification is based on their nutritive process such as parasitic, saprophytic or symbiotic. Parasitic fungi decomposes resistant celluloses, lignins which result

holes in soil and cause plant diseases. Saprophytic fungi obtain their energy causing decomposition of organic matter while symbiotic fungi live on the roots of certain plants in such a manner that both fungi and plant are mutually benefitted.

iii) ACTINOMYCETES

These are characterized by branched mycelia similar to fungi and resembles bacteria when the mycelia break into fragments. There genera of actinomycetes are well represented in the soil. Actinomycetes vary greatly in their biochemical properties, in relation to higher plants and animals and in their effect on soil bacteria.

iv) ALGAE

These are green coloured organisms and are autotrophic Their ability to produce chlorophyll makes their lives in the soil especially on its surfaces, independent of the presence of organic matter.

v) VIRUSES

Viruses are unicellular organism and are composed of specific nucleic acid surrounded by a coat of protein. They can multiply and grow only inside living cells.

SOIL MICROFAUNA COMPRISES OF THE FOLLOWING GROUPS OF ANIMALS

i) PROTOZOA : The main protozoan groups are amoebae, flagellates and ciliates, Protozoa exert a controlling effect upon the abundance of bacteria, thus affecting adversely a variety of soil processes.

ii) HIGHER ANIMAL FORMS : These include nematodes, rotifers, earthworms, larvae of insects. These organism have a variety of functions in soils. The ability of some soil inhibiting insects to attack, certain higher plants frequently makes them of great economic importance. The action of earth worms as 'soil cultivators' places them in an important category.

PHYSICO-CHEMICAL PROPERTIES OF SOIL

MECHANICAL COMPOSITION

The first information required about a soil is its mechanical composition. By mechanical composition or texture is meant the particles of various sizes such as gravel, sand, silt and clay in soils. The particle size distribute of a soil influences its chemical, physical and biological properties. Sands and gravels determine many of its mechanical properties, while clay particles, have a large surface area and determines most of its chemical and physico-chemical properties. Particle size distribution in soils influences, the water holding capacity and hence the water supply to plants. It also influences the strength and compressibility of soils. The success of any mechanical analysis depends firstly upon the preparation of the sample to ensure complete dispersion of all aggregate into their individual primary particles without breaking up the particles themselves, and secondly upon the accurate fractionation of the sample into various separates.

SOIL pH

Soil pH is an important property as it controls the availability of nutrients to plants, the bacterial activity and physical condition of the soil.

The pH is defind as $-\log_{10} aH^+$. The soil pH provides various clues about other soils properties. The soils low in pH (4 to 5) usually have high and toxic concentration of soluble aluminium and manganese. Acidity in soils arises from several different sources, like the presence of humic substances, nature of the alumino silicates in clays and their hydrolysis, presence of hydrous oxides and other soluble salts on the other hand alkaline soils with a high percentage of exchangeable sodium have a pH value above 8.5 and it may be due to the presence of sodium bicarbonate and sodium carbonate in soil as soluble salts.

ELECTRICAL CONDUCTIVITY (E.C.)

It gives an idea about the total soluble salts content in soils. Soil salinity scale based on electrical conductance of the extract. For saline soil, the salt content is more than 0.3% or E. C > 4.0 mmhos per cm. Electrical conductance of a solution increases approximately 2% per degree centigrade. Electrical conductivity of the irrigation waters may range from 0.1 to 0.75 mmho per cm or below. High salinity harzard is incurred in the case of irrigation water having conductance much above this range. The salinity is due to the presence of NaCl and Na_2SO_4 as soluble salts in soil. The saline soils has no distinct B-horizons in its profile.

EXCHANGEABLE CATIONS

The clay lattice carries a net negative charge which is compensated by cations which are located on the unit layer surfaces. In presence of water, these compensating cations have a tendency to diffuse away from the layer surface since their concentration is smaller in bulk solution. These compensating cations act as the counter ions of the double layers and are exchangeable for other cations. The major exchangeable cations on exchange sites in soils are Ca^{2+}, Mg^{2+}, H^{+}, Na^{+}, K^{+} and Al^{3+} etc. The organic cation can also replace the inorganic cations causing exchange adsorption. The proportions of exchangeable cations on the colloid surfaces are constantly changing as ions are added from dissolving minerals.

CATION EXCHANGE CAPACITY

The term base exchange capacity or'cation exchange capacity defind as the power of the soil to combine with cations in such a manner that they cannot be easily removed by simple leaching with water, but can be readily exchanged by an equivalent amount of other cations. In other words, it represents a limit beyond which the salt would be available in soils as soluble salts or in the hydrolysed state. The cation exchange capacity gives a measure about the colloidal content of the soil and their capacity to store and yield the cation needed by plants. It is one of the important criteria in identifying the clay minerals.

ESSENTIAL MAJOR AND MICRO NUTRIENTS

An element is not considered essential unless a deficiency of it makes its impossible for the plant to complete its life cycle. Of the more than 100 elements, only 16 are known to be essential for plant growth and reporduction. These elements are carbon, hydrogen, oxygen, nitrogen, phosphorous, potassium, sulfur, calcium, magnesium, iron, boron, manganese, copper, zinc, molybdenum, and chlorine.

According to the requirement of these elements by plants and soils. These are classified into two groups namely macro or major nutrients and micronutrients.

MACRO NUTRIENTS

Nine elements namely carbon, Hydrogen, oxygen, nitrogen, phosphorous, potassium, calcium, magnesium and sulfer are needed in large quantities and hence are called as macro-nutrients. Plants take up carbon as CO_2, hydrogen as H^+ and H_2O, Oxygen as O^{2-}, OH^-, CO_3^{--}, SO_4^{2-} and CO_2 mostly through leaves, nitrogen as NH_4^+ and NO_3^- , phosphorus as $H_2PO_4^-$ and HPO_4^- , potassium as K^+,Calcium as Ca^{2+} and Magnesium as Mg^{2+} Nitrogen, phosphorus and potassium are most important macro-nutrients for the proper growth of plants and are thus being supplied to meet the plants requirement in the form of chemical fertilizers.

NITROGEN

Nitrogen is the most important element in plant growth. It is a constituent of plant proteins, chlorophyll, nucleic acids, and other plant substances and hence needed in large amount.

Poor plants yields are mainly due to a deficiency of nitrogen. Under its deficiency, the leaves are small, the stems are thin and upright and lateral shoots are few. The leaves usually have a pale, yellowish green colour in the early stages of growth and many develop yellow red or purple colours at the latter stages. In addition, nitrogen increase the proportion of water (Walson, 1946) and decreases the percentage of Ca(Beeson, 1966)in plant tissues symbiotic fixation of nitrogen by legume bacteria can add 45 to 250 ponds per acre of nitrogen depending upon the type of legume plants. In a non-symbiotic fixation, certain types of micro-organisms like bacteria and blue green algae exist in soil and water, convert nitrogen into the body tissues and then release it for plant use when they die or get decomposed

Organic nitrogen deploted from the soil through oxidation and microbial activities. The rate of this loss depends upon various factors such as soil texture, soil temperature, aeration, and erosion etc. Nitrate (NO^-_3) is the most readily leached form of nitrogen while the ammonium (NH^+_4) ions which are held at cation exchange sites, resist

PHOSPHORUS

Phosphorus is the second most important element just next to nitrogen. The nucleus of each plant cell contains phosphorus and, therefore, cell division and growth are dependent upon the availability of phosphorus.

Phosphorus nutrition is doubly critical because the total supply of phosphorus in most soils is low and it is not readily available for plant use. Phosphorus is also supposed to help in high agriculture production of food grain, sugar content in the potato and corns.

Phosphorus in soil is present in both organic and inorganic forms that may vary with the organic fraction in soils. Plants utilize phosphorus in its mineral forms and hence the organic forms have to be mineralized before it is available to plants.

Acidic and alkaline reactions in soil restrict and reduce phosphorus availability. However, a pH range between 6.5 to 7.5 is ideal for its availability. The original source for phosphorus is apatite [$Ca_5(PO_4)_3F$], a calcium phosphate of low solubility. The solubilized ion ($H_2PO_4^-$) readily react with the soil ingredients like iron, aluminium and calcium and forms insoluble pohsphates. This process is called phosphate fixation. The alkali soils, tricalcium phosphate is formed, which has low solubility. Thus phosphorus is not

very mobile in soil solutions and should be applied wherever it is required in soils. Leaching losses are low.

POTASSIUM

The amount of total potassium is most soils is sufficient to last several liftimes, because some soil potassium is a constituent of very slowly soluble minerals, such as orthoclase feldspar ($KAlSi_3O_8$), so the resulting soluble potassium is only sparsely available to plants. Potassium in plants stays in a mobile form rather than as an integral part of any fixed compounds. It helps to maintain cell permeability, aids in the translocation of carbo-hydrates (Webster and Varner, 1954), keeps iron more mobile in the plant and increases the resistance to certain diseases.

Potassium occurs in both soluble and in soluble forms in the mineral matter of the soils. Three forms of potassium (K^+) is found to occur (William 1962) in soils, namely non exchangeable, fixed and very slowly available. The fixation of added potassium in soils depends upon soil texture, kind of clay mineral, intensity of drying and the level of initial exchangeable potassium.

MICRONUTRIENTS

Iron, manganese, Zinc, copper, boron, chlorine and molybdenum are known as micronutrients or trace elements

because they are required by plants in very small amounts but these are not of less importance. Their essential role is as activators in numerous enzyme systems.

Most of the micro nutrients occur as contaminant minerals in the larger masses of the common primary minerals or rocks. Soil pH, liming and phosphorus levels influence micronutrient availability. All except molybdenum are more soluble and thus more available in strongly acid media. Heavy applications of phosphates can cause deficiences in some soils, particularly of zinc or iron, by the formation of insoluble phosphates, thereby reducing soluble zinc and iron in soils. There are many interactions of micronutrients in the soil, causing the maintenance of available micro-nutrients a complex problem.

DISTRIBUTION OF SOILS IN INDIA

A knowledge of the kinds and distribution of soils is essential for a proper appraisal of their productivity and assessment of input requirements and interun relative response to them. Standard soil surveys, and their classification (Murthy et. al., 1982) assume an important role and the Benchemark soil concept helps to :

i) Provide a base for research on soil and water management and crop responses there on to inputs.

ii) Design experiments to ascertain crop responses to variables which distinguish soil series family.

iii) Provide type locations for soil classification and further studies.

National Bureau of soil survey and Land Use Planning (Nagpur, India) has made a tremendous effort in this direction and provide a brief regionwise description of the selected Bench mark soils and classified the Bench mark soils of India a into seven regions (Fig 4) as follows :

1. SOILS OF KASHMIR VALLEY

Soils of the Kashmir valley are found on two broad land forms, the Karewa tops and the lower belt. The soils have developed under temperate climatic environment. But the region has a distinct period during April to

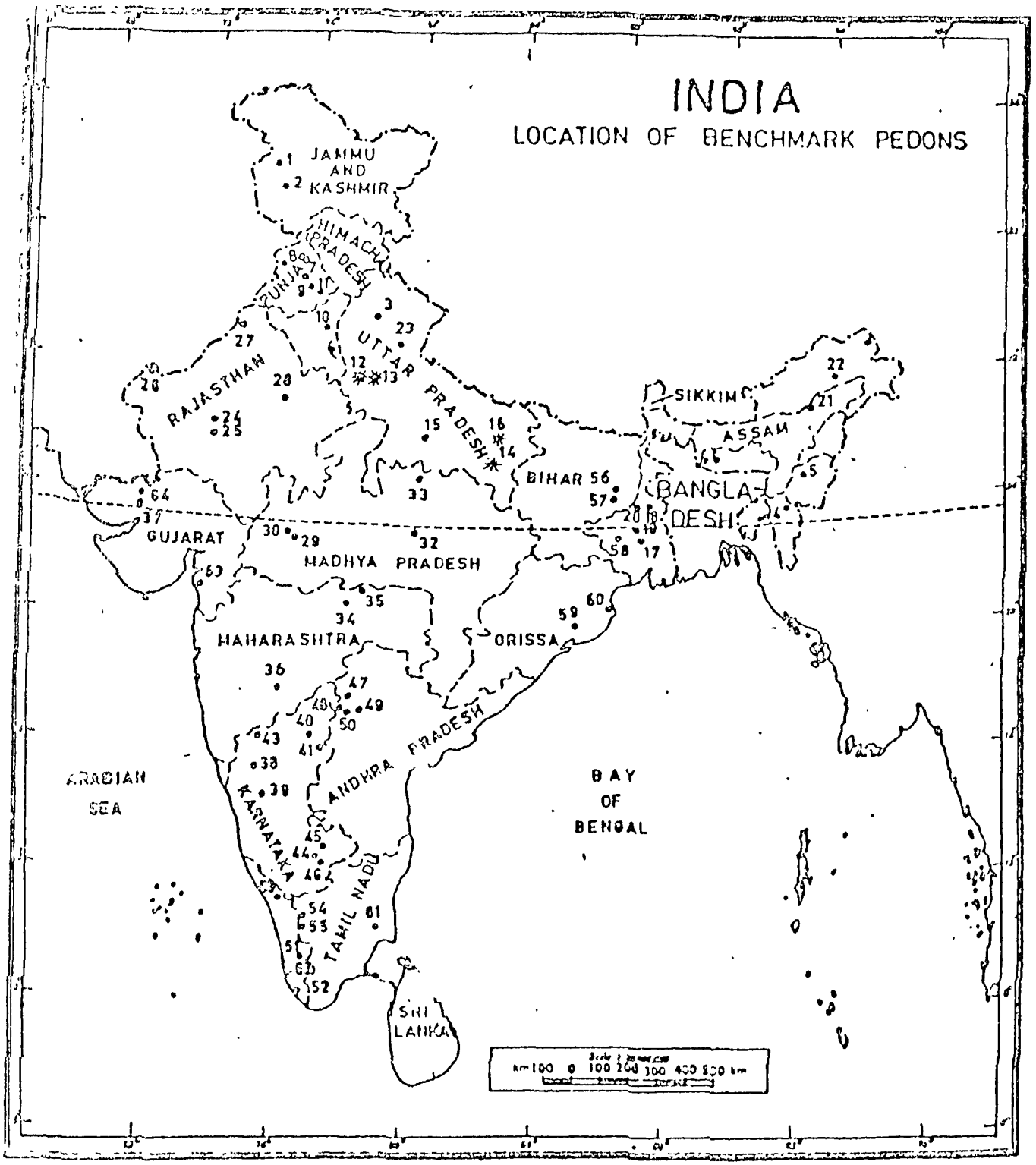


Fig. 4. Benchmark soils of India.

12. Hirapur fine sandy loam
13. Sakit sandy loam
14. Itwa silt loam
16. Bastaram silt loam

November when potential evaporation exceeds precipitation.

2, SOIL OF THE HIMALAYAN REGION AND NORTH EASTERN MOUNTAINS

This region includes the U.P. Himalayas, the eastern Himalayas, and the Purvanchal region. The soils of the region are formed on steeps hills, valleys and terraces over different geological formations, and cover large areas in subhumid warm temperate and humid tropical environments. They are susceptible to erosion.

3. SOILS OF THE INDO-GANGETIC PLAIN THE BRAHMAPUTRA VALLEY AND THE TARAI

The Indo-Gangetic plain and the Brahmaputra Valley togetner cover about 700,000 sq. km. The alluvium is very thick, and is variable according to geomorphic position and the source of the river transporting the sediments. The climatic environment ranges from semi-arid to humid subtropical. Within the region soils differs mainly because of differences in relief, drainage and parent material.

4. SOILS OF THE DESERT REGION

The Indian desert is mainly represented by gently sloping undulodi:g plains and sand dunes. The major part is covered by pleistocene and recent formations.

The desert is influenced by strong south-west resulting in acolian modification of the soils. Even though the rainfall is low, short duration biomass builds up in the desert.

5. SOILS OF THE BLACK SOIL REGION

The soils of this region are clayey in nature with montmorillonite being a dominant clay which varied from 40 to 60 percent or more. The soilsss well, shrink and crack and are also easily dispersed. They have high moisture retention capacity and potential fertility.

6. SOILS OF THE RED AND LATERITE SOIL REGION

The red and laterite soils extends in penisular India and some parts of Orissa, Bihar and West Bengal These soils have well-marked horizons of clay enrichment with a significant proportions of amorphous materials, Variation in texture, depth, colour and clay minerology results from relief and drainage differences.

7. SOILS OF THE COASTAL AND DELTAIC REGIONS

The eastern and western coastal plains are situated between eastern and western ghats and Bay of Bengal and Arabian Sea, respectively, while major delt a plains are those of the rivers, Ganga, Brahmaputra, Mahanadi, Godavari, Krishna and Cavery.

They range from extremely acid to alkaline in reaction, and from soils with low organic carbon content to those having organic horizons. They are formed under moderately well-drained to poorly drained conditions as influenced by relief and in undation.

PESTICIDES

Pesticide is a general term used for various chemicals that are employed to control pests like fungi, herbs, insects or other animal pests that attack food sources beneficial to man. The general definition for pesticide was made by Ware (1978) as follows :

'Any substance used for controlling, preventing, destroying, repelling or mitigating pests is known as pesticide.'

CLASSIFICATION OF PESTICIDES :

Pesticides can be classified into the following classes according to the target species against which they are intended to act, such as herbicide, fungicide and insecticide etc. There are also rodenticide, nematocides, acricides and weedicide etc. which are in common use.

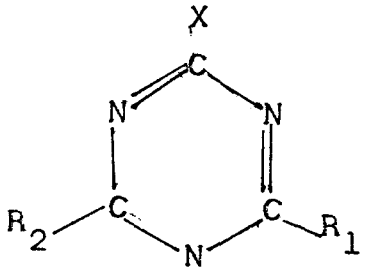
i) HERBICIDES

Herbicides are those chemicals which are used to destroy or supress the growth of unwated herbiceous and weed plants without injuring others. Organic chemicals which exhibit herbicidal and plant growth regulator properties are numerous and varied from biological, physical and chemical stand points

Important herbicides can be classified as follows :

a) S-Triazines

A general formula for S-triazine herbicide is :



where R_1 and R_2 refers to the N - substituted with lower alkyl radients and X to Cl, OCH_3 and S CH_3 etc.

Some of the commonly used S-triazine herbicides are : Simazine, Atrazine and Prometryne etc.

b) SUBSTITUTED UREAS

This class of herbicides contain a number of widely used compounds such as Fenuron, diuron and Siduron etc. These are used at high concentration rates as soil sterilants and at low rates as selective pre-and post-emergence herbicides in crop production.

c) PHENOXY ALKANOIC ACID

The members of this class of herbicides are used primarily as foliar applied treatments. Some of the important phenoxy alkanoic acid herbicides are : 2,4-D, 2,4,5-T, MCP,

MCPA and Silver etc. These are generally employed as pre.emergence treatment in conjuction with other herbicides, because of their short residual life.

Besides the above most extensive used herbicides, there are many compounds which are used as herbicides. They include : Dalapan, Propham, barban, Pyridines, Dipyridyls and many others.

The chemical characteristics of some commonly used herbicide are given in table (I).

2. FUNGICIDES

Fungicides are those chemicals which are used to control various fungi and fungus borne diseases like mildew, blights, smuts, rusts and rat etc. Fungicides broadly divided into two groups :

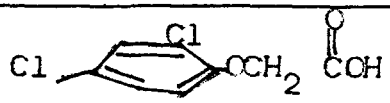
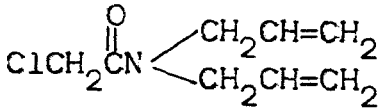
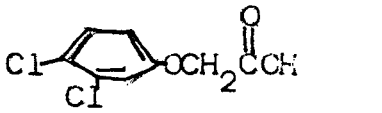
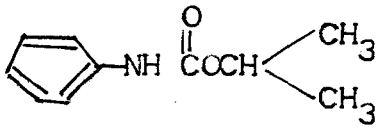
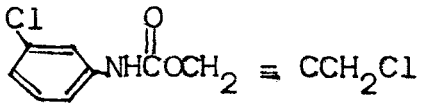
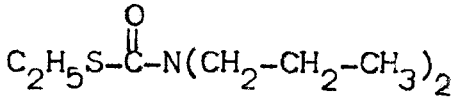
a) SURFACE FUNGICIDES

These are older fungicides used to apply to foliage as sprays or dusts. They do not enter the plant tissues but kills the fungus and the surface spores. They include : Bordeaux mixture, lime sulphur, preparations containing Cu, Zn, Mg, As, S and other naturalm plant extractions.

The organic surface fungicides are : organic mercury, alkyl mercury and phenyl mercury. They ~~are~~ appeared to cause wide spread environmental hazards due to much toxic mercury metal (Dix, 1981).

TABLE - I

CHEMICAL CHARACTERISTICS OF SOME COMMONLY USED HERBICIDES

Commercial Name	Chemical Name	Chemical structure	Toxicity
2, 4 - D	(2,4-dichlorophenoxy) acetic acid		Highly selective herbicides, So not at all toxic to other herbs or plants.
Allidochlor or CDAA	N-N-diallyl-2-chloro-acetamide		No adverse effect on human or animal health recently used mainly for control of woody perennials.
2, 4, 5 - T	(2,4,5-trichlorophenoxy acetic acid		
Propham	Isopropyl carbanilate		Kill plants by stopping cell division so, slightly toxic to other plants also.
Barban	4-Chloro-2-butynyl-m-chlorocarbanilate		Selective herbicides usually acts as a weed controlling agent they are quite volatile must be incorporated in soil after application.
E P T C	S - ethyl dipropyl thio carbamate		

b) SYSTEMIC FUNGICIDES

These fungicides are much more effective than surface fungicides because these are absorbed into the plant through leaves, roots and seeds and are translocated within the plant tissues. Commonly used systemic fungicides are : Benomyl, MBC, TB2 and carboxin etc. They have low toxicity to plants, birds and mammals.

3) INSECTICIDES

Insecticides are those substances which are used to control or kill various insects. They can be applied directly to soil or as a sprays or dust to foliage plants.

In general insecticides may be classified into following broad groups :

a) ORGANOCHLORINE

Among various organochlorine insecticides developed so far, the most important and best known is DDT. It was followed by BHC. During the recent years, a range of these insecticides were developed as chlordane, heptachlor, texaphene, aldrin dieldrin, endrin and endosulfan etc. In general, these are wide spectrum insecticides used to kill a great variety of pests.

b) ORGANOPHOSPHORUS

The organophosphorus insecticides includes : Parathion, diazinon, trichlorphon, phosrate, disulfoton, menazon and others.

c) CARBAMATES

Some carbamate compounds have also been used as insecticides. Some newly developed carbamate insecticides are inpractice nowadays. They include CPMC, carbofuran, bendiocarb, aminoacarb and meabal etc.They persis much less than organochlorines but longer than organophosphorus compounds.

These important insecticides and their chemical characteristics are given in Table II.

4) RODENTICIDES

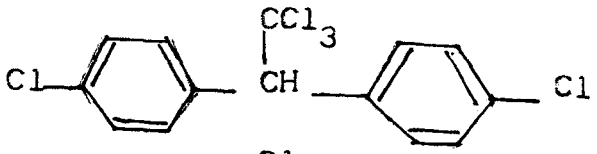
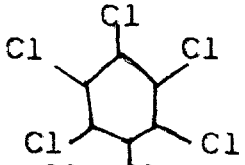
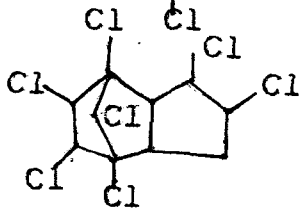
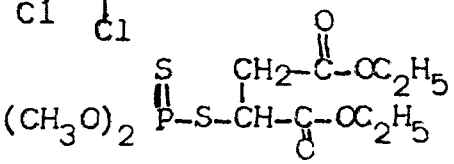
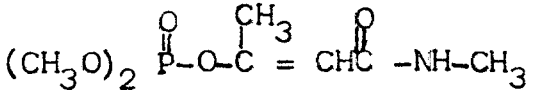
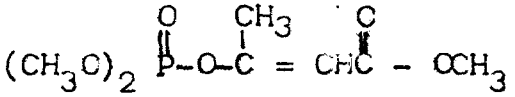
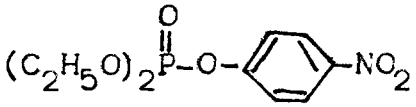
These are used for the control of certain rodents such as mice, rats, squirrel ground hogs etc. which damage property extensively and spread diseases. These includes : Calcium cyanide, Zinc phosphide, barium carbonate, α-naphthol and Warfrain etc.

5) ACRICIDES

These are used for controlling mites which are harmful to fruit trees and crops.The commonly used acricides are : aryl alkyl sulphide, chlorofension and dicofal etc.

TABLE - II

CHEMICAL CHARACTERISTICS OF SOME COMMONLY USED INSECTICIDES

Commercial Name	Chemical Name	Chemical structure	Toxicity
D D T	1,1,1-trichloro-2-2, bis (p-chlorophenyl)ethane		Highly toxic, a major threat to environmental balance.
B H C	1,2,3,4,5,6 - hexa - chlorocyclohexane		Hazardous to human and their pets, highly volatile.
Chlordane	1,2,4,5,6,7,8,8 - Octa-chloro - 3a,4,7,7a - tetrahydro-4-7-methanoindane		Highly toxic, mostly affect the nervous system of humans.
Malathion	Diethyl mercaptosuccinate S-ester with O,O,-dimethyl phosphorodithioate		Quite safe, little hazardous to humans or other pests
Monocrotophos (Azodrin)	3-Hydroxy-N-methyl-cis-crotonamide dimethyl phosphate		highest mammalian toxicity, limited use in agriculture
Mevinphos (Phosdrin)	Methyl 3-hydroxy-alpha-crotonate, dimethyl Phosphate		Highly toxic, used in commercial vegetable production.
Methyl parathion	O-O-dimethyl(O-p-nitro phenyl) phosphorothioate		Lower toxicity to human and domestic animal and broader range of insecticidal control.

6) NEMATICIDES

These are used for controlling nematodes, underground parasitics nematodes attack the root of plant and result in a general weakening of the plant leading to poor growth and yield. Some of the commonly used nematocides are nemagon, telone and oxamyl.

7) MOLLUSCICIDES

Molluscicides are compounds used to control snails, which are the intermediate hosts of parasites responsible for some diseases to humans and which feed in gardens, greenhouse, and fields, including the slugs. Formetanate, Pentachlorophenol, Metaldehyde are among the some well known molluscicides.

8) AVICIDES

All birds, in one way or another are beneficial to humans. But at some occasions this group of beautiful creatures create some problems, especially, destruction of crops, transmission of diseases etc. And their existance create a problem for the protection of crops, so some compounds employed for their destruction or killing and this group of chemical compounds known as Avicides. Some of the well known avicide are Avitral, starticide, Endrin etc.

ADSORPTION

The term adsorption is applied to the condensation of molecules on the surface of solids or liquids. Adsorption may be of two types viz physical and chemical. The physical adsorption occurs mainly due to weak forces such as ion-dipole, dipole-dipole, polarization or induced dipole vander waal's forces etc. This phenomenon is more or less non-specific, reversible and temporary in nature. While, on the other hand, chemical adsorption is due to the chemical linkage between adsorbate and adsorbent which gives rise to a permanent binding of species over adsorbent surfaces.

The clay minerals as well as crystalline and amorphous oxide and hydroxides both having a capacity for adsorption due to coulombic, and/or physical forces, adsorb the organic and inorganic species at its surfaces. The organic matter has been reported to have a highest cation exchange capacity (200 to 400 meq/100 g] and surface area (500 to 800 sq. m. per gram) and hence it is considered as the important ingradient of the soil.

The adsorption of organic molecules and pesticides on clays is governed by the colloid type, physio-chemical nature of adsorbate, pH, nature of saturating cation on the colloid exchange sites and temperature etc. Bailey et. al 1964). The physico-chemical nature of adsorbate that controls

the role of the male cule are (Greenland, 1965, Bailey et al. 1968).

(1) Chemical character, shape and configuration (2) acidity or basicity of the molecule (3) water solubility (4) charge distribution on the organic cation (5) polarity of bonds (6) molecular size, and (7) polarizability.

The adsorption of inorganic cations with soils are generally found in the order,

$H^+ > Al^{3+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+ > Li^+$.

The adsorption of these cations further increases with the increase in the concentration of their salt in soil water systems.

The property of adsorption plays an important role in soil fertility. It is due to this property that a soil is able to hold water and plant nutrients and keep them available for the use of growing plants. Soluble substances added to the soil in the form of fertilizers are retained in it because of the power of adsorption that soil colloid possesses, otherwise they would be lost from the soil through leaching. At the same time, this property enables plant nutrients to be retained in the soil in an available form.

ADSORPTION EQUATIONS

and solution concentration (Ce) at constant temperature. Gnerally, two types of isotherm equations namely, Freundlich and Lang muir equations, have most frequently been used to describe the adsorption behaviour of various species in soils.

a) FREUNDLICH EQUATION

In Freundlich type of adsorption isotherm, the concentration of solute species in adsorbed phase is given by the euqation.

$$X / m = KC_e^{1/m}$$

or

$$\ln (X/m) = \ln K + 1/n \ln Ce$$

Where X/m is the amount of solute adsorbed (X) permass of adsorbent (m), the constants K and 1/n represent the ausorption capacity and intensity, respectively, Ce is the equilibrium concentration of solute in solution.

If ln (X/m) is plotted against ln Ce, a straight line is obtained whose intercept and slope represents the constant K and 1|n respectively using the value of K as a measure of adsorption, the adsorption capacity of various adsorbent may be compared with 1|n measures the non-linearity of the process. If1|n is unity, the process is said to be linear.

b) LANGMUIR EQUATION

The Langmuir equation may be written as :-

$$X|m = \frac{ABC_e}{1+BC_e}$$

where A = adsorption maxima (ug/g),

B = Coefficients that reflects the relative rates of adsorption and desorption at equilibrium and thus, affinity terms (ml|µg), X/m and Ce are the same as the Freundlich equation.

The linear transformation of the above equation can be written as :

$$Ce\ |X|m = Ce/A + 1/BA$$

The slope and intercept of the plot (Ce|X|m Vs. Ce) gives the value of constants, 1/A and 1/BA respectively. The adsorption capacity of adsorbent(A) depends upon the specific surface area, surface charge characteristics. The constant B is a measure of the adsorption energy.

ROLE OF HEAVY METALS IN SOIL POLLUTION

Utilization of sewage sludge and industrial wastes by the application to agricultural soils as asource of micronutrients and fertilizers or as land fill gains importance during the recent years.

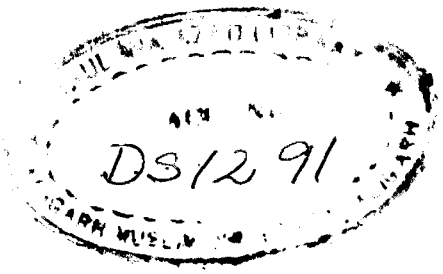
Sludge can be of immense importance as a renewable source, in helping to improve soil structure and provide a number of plant nutrients, However particular concern has been generated over the possibility of toxic elements entering the food chain or moving into the ground water system.

Studies on problems arising from heavy metal addition to soils have been made by Chaney (1973), Page (1974), and Leeper (1978). In addition, composition of different sludges and industrial have been made by various workers (Mccalla, et al. 1977, and Stover et. al. 1976). It has been found that metals e.g. Pb, Cd, Cu, Ni and Cr etc. constitute a major part of its composition, although their amounts may vary. Bloomfield and Pruden (1975), Lagerwerff et al. (1976) and many other workers have reported that numerous immobile forms of heavy metals may occur in sludges as insoluble, sorbed and organic bound forms and as their metal carbonates and sulfides.

Numerous studies on the movement of heavy metals through soils profiles have been reported (Lund et. al 1976)

Sidle et. al. 1977). In recent past, studies showed that mobilities of heavy metals are depends on the factors such as nature of soil constituents, e.g. nature and extent of clay, iron and manganese hydrous oxides and humic acid and fulvic acid etc.

The heavy metals toxicity and their mobility through soil are largely affected in the form of metal - SOM complexes The metal ions get bound with different constituents of soil organic matter which are the most reactive sites of the soil (Holtzclaw et. al. 1978, Hodgson et. al. 1965, and Sposito et. al. 1976).



HEAVY METAL INTERACTIONS IN SOIL

Most of the heavy metals soil interaction studies have been confined to deal with the adsorption, desorption, precipitation and leaching processes. It has been observed that the heavy metals are lost from soil solution through adsorption or precipitation. Cation exchange and specific adsorption are the main sources of heavy metals loss by adsorption process. In specific adsorption, the cation species are adsorbed in excess of the surface charge at high bonding strength. These sites may be located on organic and inorganic compounds manganese, aluminium, iron oxides, and soil organic matter. Various heavy metals have been reported to be specifically adsorbed over these surfaces, for example, Cu and Ni on soil organic matter (Schnitzer and Khan, 1972), Cd on freshly precipitated Fe and Al gel (Kinniburgh et. al. 1977).

MOBILITY OF HEAVY METALS IN SOILS

The movement of chemical substance in soil may influence both its effectiveness and patential as a contaminant in adjacent soil, water or air. The substance moves predominantly in vertical direction in the zone of aeration above the water table (Jordon et al., 1970). The chemical substance in soil may translocate due to two general processes namely mass transfer and diffusion. Any movement to a considerable distance is said to be occured by mass transfer i.e. flower

convection. It is caused by water percolating downward or absorption upward through soil pores. Furthermore, the soils have pores of various sizes, therefore, the mobility of a particular substance in soils varies with particle size.

Interactions with the soil itself is a highly significant factors which retards the movement of chemicals in soil. Various other factors which affects the mobility have been reported by Bailey and White (1964) and others (Rhodes et al., 1974, Schreiber et. al., 1971). Some important parameter like nature of chemical substance and soil colloids, soil pH, exchangeable cations and anions etc. have been reported (Khan et. al., 1982, Khan et. al, 1983, Grover, 1973, Singhal et al., 1977) to affect the translocation Process in soil.

METHODS FOR STUDYING HEAVY METALS MOBILITY IN SOIL

Various methods have been tried to evaluate the movement of chemical species in soil. Among the various field and laboratory studies the following two simple and inexpensive methods have been tried and standardized in recent past :

(i) SOIL COLUMNS

Most of the leaching studies in laboratory have utilized the vertical columns containing soil samples and applying substances to these columns. The water percolates through

column in downward or upward direction and mobility of chemical substances is measured by analyzing them at different heights of the column. Various conventional columns have been used by various workers. For example, aluminium rings (Harris, 1967), Stove pipe sections (Rodgers, 1968), rectangular plastic paper (Horowitz, 1968) etc.

The chemical substance is analyzed in various sections of the column. Direct analysis of column effluent (Davidson and Santelmann, 1968, Rodgers, 1968) has been carried out for highly mobile substances

(ii) SOIL THIN LAYER CHROMATOGRAPHY

Thin layer chromatography is an inexpensive, sensitive, selective and rapid tool of analytical chemistry used for separation and identification of organic and inorganic compounds (Ludwich et al., 1977, Prebyl et al., 1977). In 1968, Helling and Turner, first introduced Soil thin layer chromatography for studying the pesticide movement in soils by applying thin layers of soils on glass plates. Later in1970, Rhodes et. al. used soil TLC for the determination of mobility of agrochemicals in soil. In recent years this method provides a lot of information about the mobility of trace metals, organics, heavy metals etc. in soils and about the various factors affecting the mobilities of these chemicals (Singhal et. al,

1977, Singhal and Bansal, 1978, Khan et. al. 1982, Khan et.al. 1985).

Soil thin layer chromatography is an adsorption chromatography where the adsorbent is a thin layer of soil deposited on a glass plate. Soil component provide an adsorptive phase where adsorption and desorption take place very rapidly and reversibly. Constituents like soil organic matter further increase the adsorptive property. This makes the soil more effective as a static phase in soil TLC.

The preparation of soil TLC plates is carried out by spreading a uniform thin layer of aqueous soil slurry with the help of a conventional TLC applicator. It is then allowed to stand overnight for drying in vertical position as suggested by several workers (Brenner et. al. 1961, Michalec et al. 1962, Randearath 1962). The thickness of the layer on soil TLC plates in the range of 0.15 to 2.0 mm is important with respect to R_f for diagonastic or qualitative work (Helling, 1971). Better results are obtained if the layers are thin because the spray reagent is much more sensitive when it does not have to search for tiny amounts of substance in a large amount of adsorbent.

The amount of substance applied depends upon the layer thickness and the visualization method which are inversely

proportional to each other. The substance to be studied is normally applied by touching the tip of a filled capillary, micropipette or microburette to the adsorbent layer. The sample is placed or spotted about 3 cm above the bottom end of the plate so that the solvent level will be at least one centimeter below the centre of the spot. The diameter of the spot should not exceed 0.5 cm and should be as small as possible. These plates then developed in developing solution in a closed, saturated system, such that the bottom of the layer dips into the developing solvent. After the solvent ascends 10 to 15 cm, the plate is removed, air dried, and usually detected by some chemical reagents used as detectors, besides this fluorescence, iodine vapour, UV light and radio active scanning are the other methods of detection. The mobility is estimated as Rf value which is the ratio of the distance travelled by the substance to that of solvent (Helling, 1971).

Mobility of the chemical substances can be affected by altering the conditions of the static phase (Soils), developer and the applied substances. This provides a very large field of application of soil TLC for investigating the mobility patterns of various chemical used or found in soils.

THE PROBLEM

Sewage sludge and industrial waste application to soil are finding an increasing use in modern agricultural practices. They are, while beneficial in several ways, posing some undesirable effect on animal and plant life due to the accumulation of heavy metals. During recent years, various food plants have been studied to analyze the presence of heavy metals such as Pb, Cd, Ni, Cr and several others.

Industrial wastes, sewage sludges and fertilizers impurities and many other processes like atmospheric fallout from smelter, auto exhaust, have produced the heavy metals contamination of soil and plants. Which increase the concern over the soil pollution, and adversely effects the animal health. Inhalation and ingestion are the modes of their entry into men. Particular concern has been generated over the possibility of toxic elements entering the food chain through plants In order to devise methods for minimizing the content of these metals into food, Information is needed for the condition of their translocation through soil that may be influencing their uptake by plant.

Mobility and adsorption of heavy metals in soil provide an useful information regarding their fate in soil environment During the last few decade, a number of studies has been made on the interaction of heavy metals with soils and crops.

However, there are many areas like mechanism of their adsorption, desorption, chelation and translocation under specific conditions of the soil, which are still unexplored.

Due to the great importance attached with the heavy metals and their interactions with soils and crops, it was considered worthwhile to plan the present work on the following lines :

1. The introduction part deals with the survey of the past and present literature so as to carryout research work in the areas of heavy metal pollution in soil.

2. Studies on the heavy metals mobility in soil as affected by chemical fertilizers and pesticides.

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C H A P T E R - II

STUDIES ON THE HEAVY METALS MOBILITY IN SOIL AS AFFECTED BY CHEMICAL FERTILIZERS AND PESTICIDES

INTRODUCTION

Heavy metals in soils because of their great potentialities for crop response, have been subject of extreme importance in recent years (Valdares, et. al. 1983, Khan and Khan, 1983). It has been observed that certain heavy metals like Pb, Cr, Cu, Ni and Mn etc. Which are present in agricultural soils in traces, influence the availability of other nutrient elements to plant (Kumar et. al., 1986). It has also been studied that the chemical fertilizers and pesticides which are extensively used in agriculture now a days for healthy plant growth, significantly affect the smooth absorption of nuttients by plants.

This present study deals with role of some pesticides and chemical fertilizers on the mobility of heavy metals through soil, with a view to asses their binding tendencies with soil particles in absence and in presence of soil organic matter by using soil TLC. These result may be of immense importance in tackling the pollution caused by the toxic heavy metals in soil.

EXPERIMENTAL

The soil used in these investigations was Hirapur fine sandy loam (depth, 0-25 cm) collected from the cultivated lands of Aligarh district. The physico-chemical properties were determined as follows :

A) Determination of Mechanical Composition of Soil :

The mechanical composition of the soil sample was determined by International pipette method as given by Piper (1950). The results obtained were clay 14%, sand 61% and Silt 25%.

B) Determination of Soil pH :

The pH of the soil was recorded with Elico pH meter model LT-10 with glass and saturated colomel electrodes assembly. A 1:2.5 soil: water ratio was used for measuring the pH of the soil. The pH of soil was found to be 8.8.

C) Determination of Electrical Conductivity :

The electrical conductivity of the soil was measured with Philips conductivity bridge and dip type cell at $30\pm1^{o}C$. A 1:2.5 soil: water ratio was used for the measurement. The electrical conductivity of soil was found to be 4.5×10^{-4} mmhos cm^{-1}.

D) Determination of Organic Matter :

Method of walkley and Black (1947) was used for the determination of soil organic matter (SOM) content in the soil. The organic matter was found to be 0.41%.

E) Determination of Cation Exchange Capacity :

Cation exchange capacity was determined by the Jackson's method (1958) and CEC was found to be 7.3 meq per 100 gm of soil.

DETERMINATION OF R_f - VALUES BY SOIL THIN LAYER CHROMATOGRAPHY :

The mobility of heavy metals in terms of their R_f - values through soil was determined by soil thin layer chromatography as follows :

Apparatus : TLC applicator with adjustable thickness, Uniform glass plates (20x4 cm) glass chambers (Jars of 25 X 10 cm size) with covers, glass sprayer and a 100 mesh (B.S.S.) sieve.

Solutions and Reagent : 0.1 M nitrate solutions of Nickel, chromium, copper, Manganese and lead were prepared in distilled water and a 0.1% (W/V) solution of haematoxylin was prepared in ethanol.

Preparation of Plates : For the measurement of Rf values, the soil sample was ground and passed through 100 mesh sieve (BSS) to obtain a homogeneous particle Size (< 150μ).

A soil slurry was prepared in distilled water with a soil water ratio of 1:2. Glass plates were cleaned with detergent solution, water, and with 50% methanol water acidified with hydrochloric acid, and finally the plates were wiped with cotton soaked with hexane. These glass plates were coated with slurries of soil sample to a thickness of 0.5 mm with the help of a conventional TLC applicator. The prepared plates were kept on a rack and were allowed to dry at room temperature overnight. Two lines at 4 cm and 14 cm above the base were scribed so that a distance of 10 cm used for development of all the plates.

Application of Samples and Development of Plates :

About 6 μl nitrate solution (0.1M) of heavy metals was applied on the base line of TLC plate in a single applicatio with the help of micropipette so that the diameter of the spot not exceeded 0.5 mm. TLC plates were then developed with distilled water up to upper line on the plates in the closed glass chambers by ascending chromatography. To prevent distintegration of soil in contact with water, wet stripes of filter paper about 2.5 cm wide were wrapped around the bottom of the plate before the development.

Drying and detection : The developed plates were air dried at room temperature Pb^{2+}, Ni^{2+}, Mn^{2+} and Cu^{2+} were detected as violet colour spot of metal - haemotoxylene complexes by spraying 0.1% (W/V) ethanolic solution of haematoxylene. Whereas Cr^{3+} detected as bright yellow spot.

Measurement of Rf - Value : The R_f -values (mobility) were measured by the relations :

$$R_f \text{ - Value} = \frac{\text{Frontal distance moved by the metal}}{\text{Frontal distance moved by the developer}}$$

FOR THE EFFECT OF ORGANIC MATTER :

Two set of all experiments were conducted to study the effect of soil organic matter on the mobility of heavy metals. One of soil sample was natural with organic matter but in other experiments soil organic matter was decomposed by 30% H_2O_2.

FOR THE EFFECT OF FERTILIZERS AND PESTICIDES :

Effect of fertilizers and pesticides were studied by mixing their known quantities in soil thoroughly and then this amended soil was applied on glass plates and developed as described earlier.

STATISTICAL ANALYSIS :

All experiments were done in triplicate and data obtained were subjected to statistical analysis, critical

difference (C.D) calculated at 5% level of significance by the method given by Panse and Sukhatme (1978).

RESULT AND DISCUSSION

An examination of Table III shows that the mobility of heavy metals through soil is less in the presence of soil organic matter as compared to the soil with decomposed organic matter. This may be due to the high adsorptive power of the soil organic matter (SOM) bound with the clay particles. The mobility of heavy metals follows the order Ni > Mn > Cr, > Cu > Pb. This trend is found in the reverse order of their binding capacities with soil organic matter (Stevenson and Ardakani, 1972, Lund et. al. 1976, Khan et. al. 1982).

An application of chemical fertilizers such as, Urea, Ammonium phosphate, Ammonium sulphate and potassium chloride were found to increase the mobility of Ni, Cr and Mn to a considerable extent (Fig. 5), While mobilities of Pb and Cu remained unaffected throughout the range of fertilizer application except in the case of ammonium sulphate where Cu showed an increase at only initial level of fertilizer application. The mobility order was Ni > Mn > Cr → Cu > Pb in all cases of fertilizers application except in the case of potassium chloride where order was Mn > Ni > Cr > Cu > Pb. These results can be explained on the basis of the following

TABLE - III

THE EFFECT OF ORGANIC MATTER ON THE MOBILITY OF HEAVY METALS THROUGH SOIL AND SOLUBILITY OF THE METAL CHLORIDES SULPHATES AND PHOSPHATES IN WATER AT 20°C*

Heavy metals Ions	Rf-Values		Solubility in water (g 100 g^{-1})		
	Soil with organic matter	Soil without organic matter	Metal Chlorides	Metal Sulphates	Metal Phosphates
Ni^{2+}	0.30	0.42	64.2	65.52	V.S.
Mn^{2+}	0.29	0.40	72.3	52.00	....
Cr^{3+}	0.28	0.36	58.5	12.35	Soluble
Cu^{2+}	0.07	0.22	-	14.35	insoluble
Pb^{2+}	0.06	0.14	0.99	0.00425	0.000014

* Weast and Selby (1966)

V.S. = Very soluble

TABLE - IV

EFFECT OF UREA ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Meavy Metals Ions	R_f - Values					C.D.*
	Conc. of Urea (%)					
	0.0	0.1	0.2	0.3	0.4	
Ni^{2+}	0.30(0.42)	0.41(0.53)	0.60(0.66)	0.70(0.73)	0.76(0.80)	0.01(0.09)
Mn^{2+}	0.29(0.40)	0.35(0.52)	0.48(0.60)	0.50(0.67)	0.56(0.75)	0.02(0.08)
Cr^{3+}	0.28(0.36)	0.31(0.50)	0.45(0.55)	0.48(0.61)	0.52(0.66)	0.02(0.03)
Cu^{2+}	0.07(0.22)	0.09(0.25)	0.08(0.25)	0.10(0.25)	0.10(0.25)	0.02(0.04)
Pb^{2+}	0.06(0.14)	0.08(0.15)	0.08(0.15)	0.07(0.14)	0.06(0.13)	0.02(0.03)

* Critical difference at 5% confidence limit.

R_f - Values in soil with decomposed organic matter are given in paranthesis.

TABLE - V

EFFECT OF AMMONIUM PHOSPHATE ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f -Values					C.D.*
	Conc. of Amm. Phosphate (%)					
	0.0	0.1	0.2	0.3	0.4	
Ni^{2+}	0.30(.0.42)	0.46(0.45)	0.50(0.52)	0.53(0.66)	0.55(0.66)	0.05 (0.05)
Mn^{2+}	0.29(0.40)	0.43(0.40)	0.46(0.50)	0.49(0.52)	0.50(0.55)	0.05 (0.02)
Cr^{3+}	0.28(0.36)	0.40(0.40)	0.41(0.42)	0.45(0.48)	0.50(0.50)	0.06 (0.04)
Cu^{2+}	0.07(0.22)	0.11(0.25)	0.07(0.23)	0.11(0.20)	0.10(0.25)	0.04(0.03)
Pb^{2+}	0.06(0.14)	0.06(0.12)	0.03(0.15)	0.05(0.18)	0.07(0.17)	0.05(0.03)

* Critical difference at 5% confidence limit.

R_f - Value in soil with decomposed organic matter are given in paranthesis.

TABLE - VI

EFFECT OF AMMONIUM SULPHATE ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metal Ions	R_f-Value Conc. of Ammonium Sulphate (%)					C.D.*
	0.0	0.1	0.2	0.3	0.4	
Ni^{2+}	0.30(0.42)	0.65(0.71)	0.70(0.75)	0.74(0.84)	0.80(0.88)	0.05(0.05)
Mn^{2+}	0.29(0.40)	0.55(0.60)	0.57(0.62)	0.66(0.68)	0.68(0.75)	0.04(0.03)
Cr^{3+}	0.28(0.36)	0.60(0.65)	0.62(0.70)	0.61(0.76)	0.71(0.80)	0.06(0.03)
Cu^{2+}	0.07(0.22)	0.25(0.40)	0.23(0.37)	0.25(0.35)	0.27(0.40)	0.07(0.02)
Pb^{2+}	0.06(0.14)	0.05(0.09)	0.04(0.13)	0.05(0.15)	0.05(0.19)	0.01(0.03)

* Critical difference at 5% confidence limit.

R_f - Values in soil with decomposed organic matter are given in paranthesis.

TABLE - VII

EFFECT OF POTASSIUM CHLORIDE ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f-Value					C.D*
	Conc. of Potassion chloride (%)					
	0.0	0.1	0.2	0.3	0.4	
Ni^{2+}	0.30(0.42)	0.68(0.70)	0.72(0.75)	0.73(0.78)	0.75(0.80)	0.03(0.03)
Mn^{2+}	0.29(0.40)	0.69(0.78)	0.77(0.85)	0.80(0.90)	0.82(0.92)	0.03(0.01)
Cr^{3+}	0.28(0.36)	0.55(0.60)	0.60(0.65)	0.65(0.67)	0.69(0.70)	0.05(0.01)
Cu^{2+}	0.07(0.22)	0.10(0.31)	0.09(0.29)	0.11(0.20)	0.10(0.24)	0.01(0.02)
Pb^{2+}	0.06(0.14)	0.06(0.15)	0.05(0.15)	0.08(0.10)	0.10(0.15)	0.02(0.05)

* Critical difference at 5% confidence limit.

R_f - Values in soil with decomposed organic matter are given in paranthesis.

TABLE - VIII

EFFECT OF MALATHION ON THE MOBILITY (R_f - Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f-Value					C.D*
	Conc. of Malathion (%)					
	0.00	0.01	0.05	0.1	1.0	
Ni^{2+}	0.30(0.42)	0.42(0.71)	0.50(0.77)	0.31(0.40)	0.17(0.19)	0.03(0.04)
Mn^{2+}	0.29(0.40)	0.38(0.60)	0.35(0.65)	0.28(0.35)	0.18(0.29)	0.01(0.05)
Cr^{3+}	0.28(0.36)	0.31(0.61)	0.41(0.66)	0.21(0.35)	0.10(0.16)	0.03(0.05)
Cu^{2+}	0.07(0.22)	0.30(0.40)	0.25(0.43)	0.15(0.15)	0.09(0.10)	0.03(0.05)
Pb^{2+}	0.06(0.14)	0.14(0.30)	0.16(0.34)	0.08(0.05)	0.00(0.05)	0.02(0.02)

* Critical difference at 5% confidence limit.

R_f Values in soil with decomposed organic matter are given in paranthesis.

TABLE - IX

EFFECT OF DICHLOROVOS ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f-Value					C.D*
	Conc. of Dichlorovos (%)					
	0.00	0.01	0.05	0.1	1.0	
Ni^{2+}	0.30(0.42)	0.51(0.80)	0.19(0.68)	0.10(0.35)	0.10(0.36)	0.05(0.06)
Mn^{2+}	0.29(0.40)	0.40(0.68)	0.20(0.51)	0.08(0.22)	0.05(0.19)	0.08(0.01)
Cr^{3+}	0.28(0.36)	0.38(0.66)	0.18(0.55)	0.12(0.20)	0.10(0.28)	0.63(0.03)
Cu^{2+}	0.07(0.22)	0.20(0.37)	0.05(0.20)	0.06(0.05)	0.05(0.03)	0.03(0.00)
Pb^{2+}	0.06(0.14)	0.06(0.20)	0.05(0.05)	0.00(0.00)	0.00(0.00)	0.00(0.04)

* Critical difference at 5% confidence limit.

R_f-Values in soil with decomposed organic matter are given in paranthesis.

TABLE - X

EFFECT OF THIOMETON ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f-Value					C.D*
	Conc. of Thiometon (%)					
	0.00	0.01	0.05	0.01	1.0	
Ni^{2+}	0.30(0.42)	0.41(0.59)	0.50(0.62)	0.32(0.28)	0.10(0.15)	0.03(0.05)
Mn^{2+}	0.29(0.40)	0.40(0.51)	0.38(0.42)	0.21(0.20)	0.19(0.20)	0.01(0.03)
Cr^{3+}	0.28(0.36)	0.35(0.62)	0.40(0.60)	0.20(0.17)	0.06(0.09)	0.02(0.01)
Cu^{2+}	0.07(0.22)	0.17(0.28)	0.14(0.25)	0.09(0.05)	0.00(0.02)	0.01(0.01)
Pb^{2+}	0.06(0.14)	0.15(0.30)	0.16(0.30)	0.05(0.07)	0.00(0.00)	0.01(0.02)

* Critical difference at 5% confidence limit.

R_f-Values in soil with decomposed organic matter are given in paranthesis.

TABLE - XI

EFFECT OF TRICHLOROACETIC ACID ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f-Value					C.D*
	Conc. of Trichloroacetic acid(%)					
	0.0	0.1	0.5	1.0	5.0	
Ni^{2+}	0.30(0.42)	0.45(0.55)	0.63(0.62)	0.81(0.84)	0.90(0.90)	0.03(0.03)
Mn^{2+}	0.29(0.40)	0.31(0.54)	0.61(0.62)	0.53(0.70)	0.61(0.81)	0.03(0.01)
Cr^{3+}	0.28(0.36)	0.41(0.50)	0.59(0.60)	0.70(0.69)	0.75(0.74)	0.02(0.08)
Cu^{2+}	0.07(0.22)	0.25(0.28)	0.30(0.30)	0.40(0.30)	0.45(0.45)	0.00(0.02)
Pb^{2+}	0.06(0.14)	0.11(0.21)	0.15(0.26)	0.17(0.30)	0.20(0.30)	0.08(0.02)

* Critical difference at 5% confidence limit.

R_f-Values in soil with decomposed organic matter are given in paranthesis.

TABLE- XII

EFFECT OF p-CHLOROPHENOXY ACETIC ACID ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f-Value					C.D*
	Conc. of p-chlorophenoxy a.a(%)					
	0.0	0.1	0.5	1.0	5.0	
Ni^{2+}	0.30(0.42)	0.45(0.60)	0.56(0.67)	0.60(0.77)	0.70(0.85)	0.01(0.02
Mn^{2+}	0.29(0.40)	0.540(0.51)	0.50(0.59)	0.55(0.64)	0.60(0.71)	0.00(0.03
Cr^{3+}	0.28(0.36)	0.37(0.60)	0.45(0.62)	0.53(0.72)	0.64(0.79)	0.02(0.04
Cu^{2+}	0.07(0.22)	0.22(0.40)	0.32(0.50)	0.36(0.59)	0.40(0.65)	0.02(0.03
Pb^{2+}	0.06(0.14)	6.00(0.20)	0.02(0.25)	0.07(0.27)	0.02(0.30)	0.02(0.03

* Critical difference at 5% confidence limit.

R_f-Values in soil with decomposed organic matter are given in paranthesis.

TABLE - XIII

EFFECT OF β-NAPHTHOXY ACETIC ACID ON THE MOBILITY (R_f-Value) OF SOME HEAVY METALS THROUGH SOIL

Heavy Metals Ions	R_f-Value					C.D*
	Conc. of β-naphthoxy a.a. (%)					
	0.0	0.1	0.5	1.0	5.0	
Ni^{2+}	0.30(0.42)	0.45(0.61)	0.61(0.69)	0.65(0.80)	0.70(0.88)	0.02(0.01)
Mn^{2+}	0.29(0.40)	0.40(0.50)	0.49(0.51)	0.55(0.60)	0.65(0.68)	0.02(0.00)
Cr^{3+}	0.28(0.36)	0.35(0.41)	0.40(0.50)	0.47(0.55)	0.55(0.60)	0.04(0.03)
Cu^{2+}	0.07(0.22)	0.15(0.25)	0.19(0.25)	0.25(0.30)	0.25(0.30)	0.01(0.00)
Pb^{2+}	0.06(0.14)	0.00(0.10)	0.00(0.08)	0.00(0.05)	0.00(0.02)	0.00(0.00)

* Critical difference at 5% confidence limit.

R_f-Values in soil with decomposed organic matter are given in paranthesis.

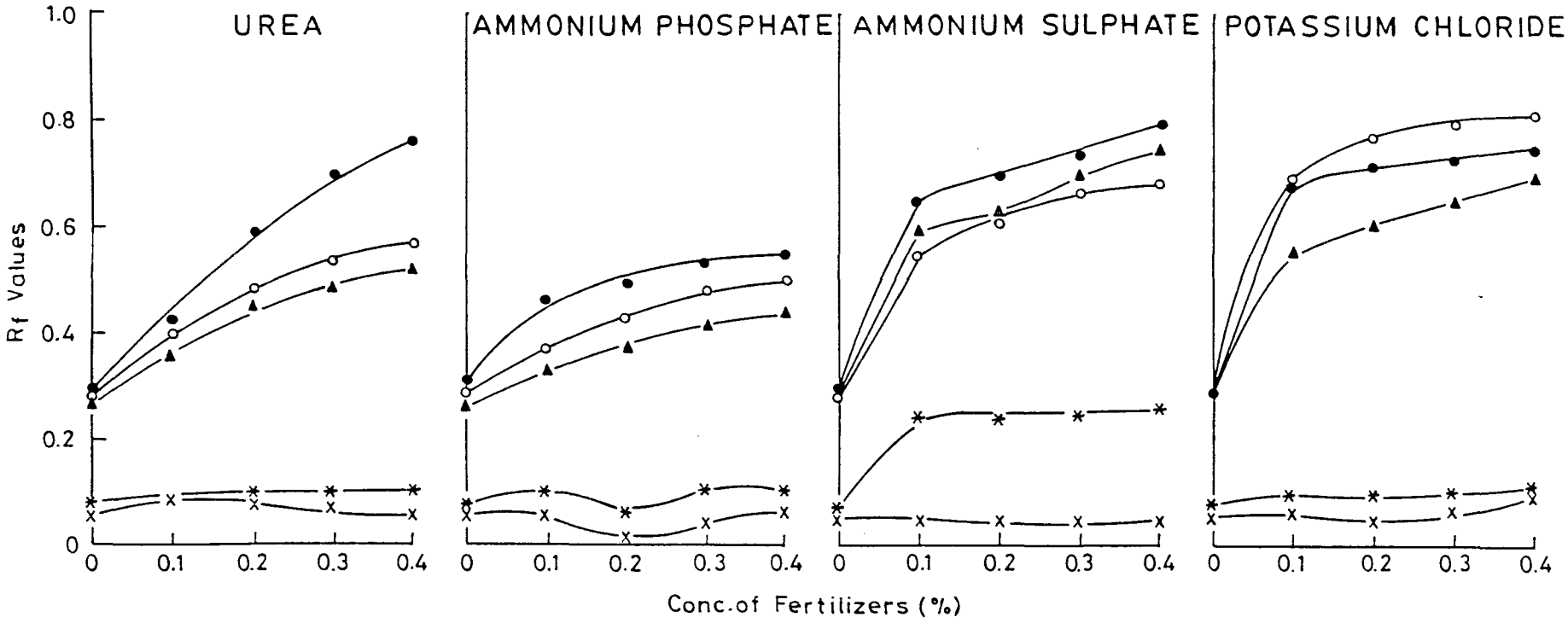

FIG. 5 EFFECT OF FERTILIZERS ADDITION TO SOIL ON THE MOBILITY OF HEAVY METALS IN SOIL

● Ni, ○ Mn, ▲ Cr, * Cu, x Pb

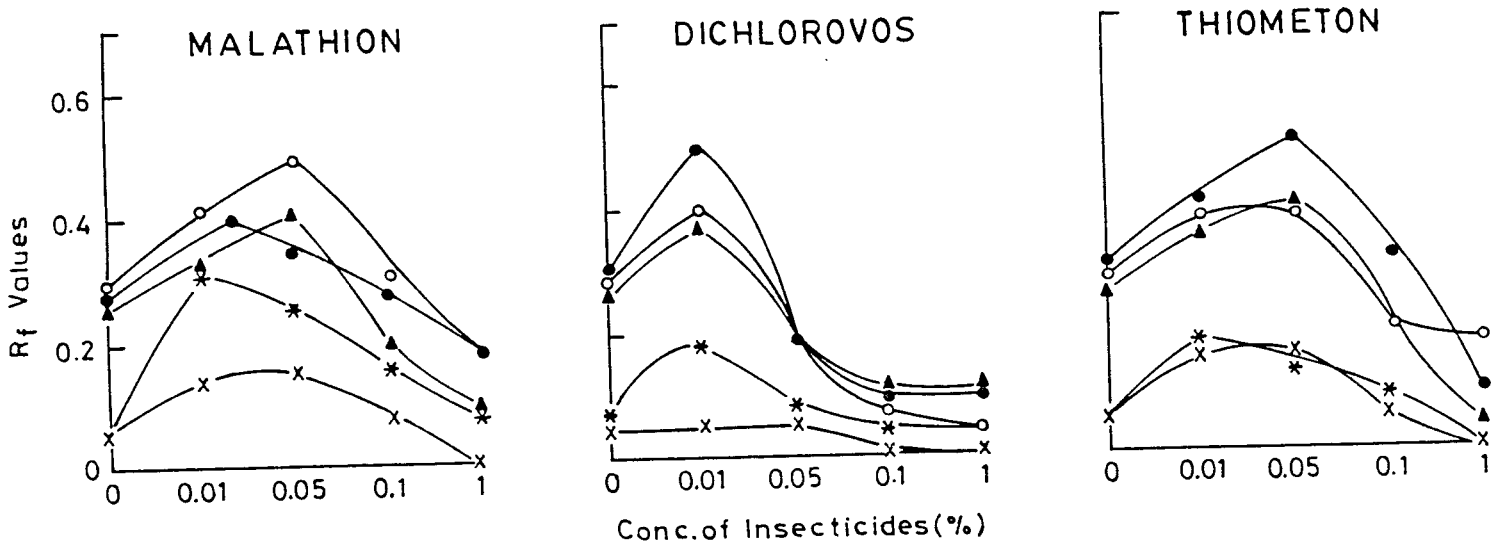

FIG.6 EFFECT OF INSECTICIDES ADDITION TO SOIL ON THE MOBILITY OF HEAVY METALS IN SOIL

●Ni, ○Mn, ▲Cr, ✱Cu, xPb

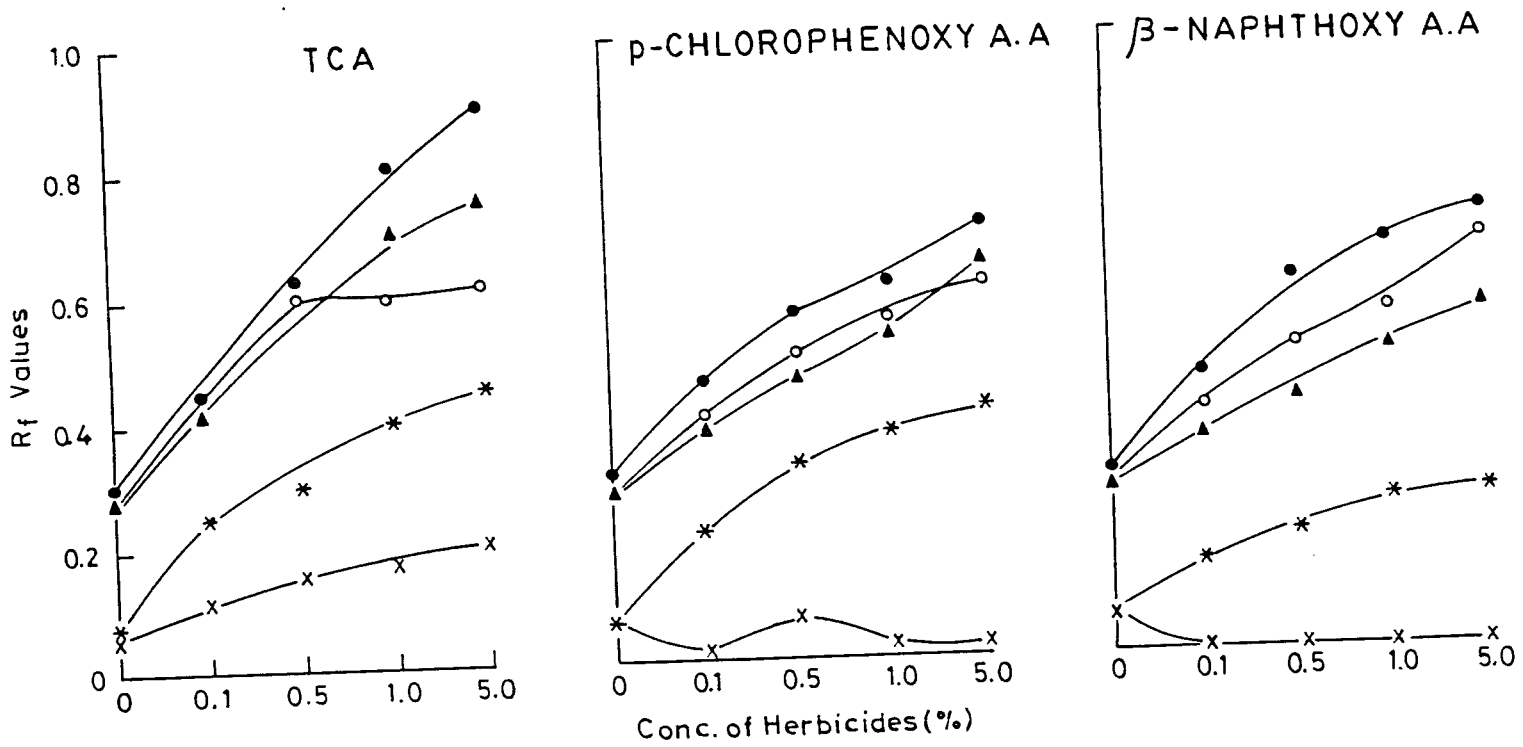

FIG. 7 EFFECT OF THE HERBICIDES ADDITION TO SOIL ON THE MOBILITY OF HEAVY METALS IN SOIL

● Ni, ○ Mn, ▲ Cr, * Cu, x Pb

reaction mechanism. Various chemical fertilizers in aqueous soil solution may be either dissociated or decomposed as :

$$KCl \longrightarrow K^+ + Cl^- \quad \text{(i)}$$

$$NH_2,CO,NH_2 + 2H_2O \dashrightarrow 2NH_4^+ + OH^- + CO_2 \quad \text{(ii)}$$

$$(NH_4)_2\,SO_4 \longrightarrow 2NH_4^+ + SO_4^{2-} \quad \text{(iii)}$$

$$(NH_4)_3\,PO_4 \longrightarrow 3NH_4^+ + PO_4^{3-} \quad \text{(iv)}$$

$$\text{Adsorption sites}^{\ominus} + NH_4^+ \longrightarrow \text{Adsorption sites}\text{-}NH_4^+ \quad \text{...(v)}$$

$$\text{Adsorption sites}^{\ominus} + K^+ \longrightarrow \text{Adsorption sites}\text{-}K^+ \quad \text{..(vi)}$$

In the above (1) to (iv) reactions, the NH_4^+ and K^+ ions are released from the decomposition of fertilizers and are added to soil. These ions are adsorbed on the adsorptive sites of the soil colloids according to equations V and VI. Hence heavy metals become free to move through soil as soluble salts of respective fertilizers anions (Table III) and show increased mobility.

It has also been observed that the effect of added fertilizers follows the order : $(NH_4)_2SO_4$ > KCl > NH_2CONH_2> $(NH_4)_3\,PO_4$ which is according to their combined effect of dissociation constant and solubility in water.

The effect of organophosphorus insecticides namely malathion, thiometon and dichlorovos on the mobility of heavy

metals in soil (vide Fig. 6) showed the mobility of heavy metals increases at the initial level (0-0.05%) of pesticides applications except in the case of dichlorovos which increases the mobility upto its 0.01% addition. The initial increase may be due to the adsorption and blocking of the reactive sites of the soil colloids. Thus, the heavy metals becomes free to move. But as the concentration of these pesticides increased the mobility of heavy metals decreased considerably. As their concentration increased they reacts with heavy metals and becomes immobile due to their low solubility in water. The possible mechanism can be proposed as follows :

Clay-Organic Complex $-M^{+}-OH + O - X \longrightarrow$ Clay - organic complex $-\overset{+}{M}-OH-O-X$

$$\bar{M}^{+} - OH + O - X \longrightarrow \bar{M}^{+} - OH \ldots\ldots\ldots O - X$$

Where $- \overset{+}{M} -$ = metalions on the adsorption sites

$- \bar{M}^{+} -$ = Heavy metal ion

Since the pH of the soil is 8.8, hence metal ions remains in their hydrated form and Hydrogen bonding as above is quite possible to occur.

In the case of substituted acetic acid herbicides, namely, Tricholoro acetic acid, p-chlorophenoxy acetic

acid and β-Naphthoxy acetic acid, the mobility of heavy metals increases throughout the range of their addition (Fig. 7) which may be attributed to the solubility of their complexes with heavy metal ions. Again, the mobility of heavy metals in herbicides amended soil follows the order Ni > Mn > Cr > Cu > Pb. It may be explained on the basis of their solubility and complexing nature of these heavy metals. In our previous report (Khan et. al., 1985), we have observed that the nature and extent of heavy metals complexation with organic substances enhance the mobility because of their movement as their heavy metal organic matter complexes. The present study substantiate our previous results.

CONCLUSION

This study shows that the mobility of heavy metal ions increases on the application of Fertilizers and pesticides to soil.

It suggestes that :

a) The city and industrial waste water should be analysed first prior to their application to agricultural land to determine their composition.

b) Waste water which contain nutrient elements like Cu, Mn and Fe etc. can be applied to agricultural soil in presence of fertilizer and pesticides in soil.

c) If waste water contains toxic heavy metals like Ni, Cr and Pb etc., they should first be removed because they have comparably increasing mobility in soil with nutrient elements and can enhance the risk of contamination of agricultural products.

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